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(54) Title: PROCESS FOR THE PRODUCTION OF AROMATIC POLYCARBAMATES

(57) Abstract: A process for the preparation of an aromatic polycarbamate which comprises reacting an aromatic polyamine, urea and an alcohol, characterised in that the alcohol is an alkoxylated monoalcohol.

PROCESS FOR THE PRODUCTION OF AROMATIC POLYCARBAMATESDESCRIPTION

5 The present invention relates to a process for the production of aromatic polycarbamates from aromatic polyamines, urea and an alcohol.

Processes for preparing carbamates by reacting amines with urea in the presence of an alcohol have been described in the art.

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In US-A 2.677.698 a process is described for the preparation of N-monosubstituted carbamic acid esters which comprises reacting a primary amine with urea to prepare a 1,3-disubstituted urea which is separated from unreacted amine, urea and generated ammonia and then reacted in a
15 second step with a mono-hydroxy alcohol to give the resultant N-monosubstituted carbamic acid ester.

US-A 2.409.712 concerning the pyrolysis of N-alkyl carbamic alkyl esters discloses a method for the preparation of such carbamic esters by
20 reacting urea, an amine such as laurylamine or beta (isobutoxymethoxy)ethylamine and alcohols such as ethoxyethoxyethanol to give the N-alkyl carbamic alkyl esters.

In EP-A 18.586 aliphatic, cycloaliphatic, arylaliphatic and aliphatic-cycloaliphatic N-substituted di- and polyurethanes are prepared by
25 reacting primary aliphatic, cycloaliphatic, arylaliphatic or aliphatic-cycloaliphatic di- or polyamines with urea and alcohol. The yield obtained when converting hexanediamine to the corresponding carbamate using butanol or octanol was at least as high as when using 2-butoxy-
30 ethanol.

In EP-A 18.588 the N-unsubstituted carbamate based on 2-butoxyethanol was used to make a carbamate from hexanediamine. The use of the N-unsubstituted carbamates of butanol or octanol resulted in slightly
35 higher yields.

EP-A 27.940 discloses the conversion of aniline and 4-methoxyaniline to the corresponding carbamate using 2-butoxyethanol in the presence of a catalyst.

40

US-A 5.453.536 discloses the pyrolysis of polycarbamates into polyisocyanates and secondary alcohols.

While these processes have their advantages, there is a continuous need
5 for a simple, economical process for preparing aromatic polycarbamates via this route.

According to the present invention there is thus provided an alternative
10 process for the preparation of aromatic polycarbamates which comprises reacting an aromatic polyamine with urea and an alkoxyated monoalcohol, with high yields of aromatic polycarbamates and high conversion rates of the reactants and short reaction times, even in the absence of a solvent and/or catalyst.

The invention thus concerns a process for the production of aromatic polycarbamates by reaction of aromatic polyamines with urea and an alcohol, characterised in that the alcohol is an alkoxyated monoalcohol.

Preferably, the alkoxyated monoalcohol used has the structure $\text{HO}-\text{CHR}^1(\text{CR}^2\text{R}^3-\text{O})_x\text{R}^4$ wherein x is an integer between 1 and 250 and $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ each are independently H or hydrocarbon radicals.

The term 'polyamines' as used herein refers to compounds having more than 1 amine group.

Suitable aromatic polyamines include, for example, 3,3'-dimethyl-4,4'-diphenyldiamine, phenylenediamines, 2,4'- and 4,4'-methylenedianiline, sulfonyldianilines, thiodianilines, diaminodiphenylmethanes and higher homologs polyaminopolyphenylmethanes, toluediamines, m-phenylene diamine, 1,5-naphthylenediamine and the like, and mixtures thereof.

Preferred are aromatic diamines or higher functionality polyamines like toluediamines, diaminodiphenylmethanes or polyaminopolyphenylmethanes or any mixtures thereof.

Any mixtures of aromatic dicarbamates and higher functionality polycarbamates may be obtained depending on the composition of the starting amine compound.

Although any alkoxyated monoalcohol of the abovementioned structure can be used in the present process, the group of alcohols according to the above formula wherein $x=1$ have proven particularly useful.

Alcohols which are thus preferably employed in at least stoichiometric amounts based on the aromatic primary amine are, for example, 2-methoxyethanol, 2-ethoxyethanol, 2-ethoxycyclopropanol, 2-isopropoxyethanol, 1-methoxy-2-propanol, 2-methoxy-3-propanol, 2-methoxy n- and iso-butyl alcohols, 2-methoxy amyl alcohol, 2-methoxyhexanol, 2-methoxy heptanol, 2-methoxyoctanol, 2-methoxy nonanol, 2-methoxydecanol, 2-methoxy 2-ethyl hexanol, 2-methoxy 2-methyl pentanol, 2-methoxy 2-ethyl-1-butanol, 2-methoxy 3,5-dimethyl-1-hexanol, and the like.

Particularly preferred alcohols are 2-methoxyethanol, 2-ethoxyethanol, 2-isopropoxyethanol, 1-methoxy-2-propanol, or mixtures thereof.

Although small amounts of a catalyst, i.e. between about 0.1 to 5.0 mole percent, based on the aromatic polyamine may be added to the reaction mixture if desired, it was found that even in the absence of a catalyst high yields of aromatic carbamates were obtained. A catalyst-free process is thus preferred.

Although the process of the invention is preferably carried out using the alkoxyalcohol as the reaction solvent, as well as reactant, other solvents or mixtures of solvents which are stable and substantially chemically inert to the components of the reaction system may be employed as a co-solvent in the reaction system if desired. Suitable inert solvents which may be employed, and generally in amounts of up to 50 weight percent based on the reaction mixture, include, for example, aromatic hydrocarbons such as benzene, halogenated aromatic hydrocarbons such as monochlorobenzene, ortho-dichlorobenzene or 1-chloronaphthalene, alkylated aromatic hydrocarbons like toluene, xylene, ethylbenzene, cumene or tetrahydronaphthalene, other functionalised aromatic hydrocarbons such as anisol, diphenylether, ethoxybenzene, benzonitrile, 2-fluoroanisole, 2,3-dimethylanisole or trifluorotoluene, alkanes such as n-pentane, n-hexane, n-heptane or higher or branched alkanes, cyclic alkanes like cyclopentane, cyclohexane or derivatives thereof, halogenated alkanes like chloroform, dichloromethane, carbontetrachloride, and alkanes with other functional groups like diethylether, acetonitrile, dioxane or

mixtures thereof, and the like

Examples of preferred solvents are halogenated aromatic hydrocarbons. Particularly preferred are monochlorobenzene and ortho-dichlorobenzene.

The ratio of reactants may be varied over any convenient range. In general, the mole ratio of amine to urea may be between about 1:1 to 1:20, preferably between about 1:1.2 to 1:10, and more preferably between about 1:1.2 and 1:5. It is generally more convenient and preferred to employ the reactant alcohol as reaction solvent and thus in excess of the stoichiometric quantity required for the reaction. Amounts of up to 50 molar excess based on the amine employed may be conveniently employed.

The reaction conditions largely depend on the type of reactants used, but are chosen so that substantially all of the amines are converted into the corresponding carbamates.

The reaction of the present invention will proceed at temperatures of from about 100 to 250°C. It is generally preferred to operate the process at temperatures of from about 150 to 220°C to obtain a convenient rate of reaction. The reaction temperature will depend on the particular aromatic polycarbamate being produced and should be below the temperature at which significant decomposition of the product might occur.

The process of the present invention is generally carried out at atmospheric pressure, although higher pressures of up to 50 bar may be used and especially at the higher reaction temperatures or when the reaction temperature is above the boiling point of the alcohol and/or reactant amine. Subatmospheric pressures may be employed, if desired.

The reaction between the urea, alcohol and the aromatic polyamine may be carried out in any suitable reactor, such as an autoclave, which is generally equipped with a means for agitation, means for regulating temperature and pressure and means for removing by-product ammonia, and possibly alcohol vapor. Although the order of addition of the reactants, and optional solvents and catalyst components may vary, a general procedure for carrying out the reaction is to charge the urea, aromatic polyamine, alcohol, inert solvent and catalyst if used into

the reaction vessel and then heat the mixture to the desired temperature at atmospheric pressure or higher pressures, if required. The reaction can be carried out batchwise, semicontinuous, or as a continuous process. The reaction products are recovered and treated by any conventional method, such as distillation or fractionation to effect separation of the aromatic polycarbamates from unreacted starting material, and optionally catalyst, solvent and by-products.

Ammonia resulting from the reaction must be removed during the course of the reaction, otherwise reduced yields of product carbamate are obtained. When the reaction is carried out at one atmosphere the ammonia is simply allowed to escape from the reaction vessel. In reactions where elevated pressures are employed provisions must be made to remove ammonia. A simple, convenient method is to strip the ammonia from the reactor with a dry inert gas, such as nitrogen and/or with the resulting alcohol vapor provided the alcohol employed is volatile at the reaction temperature. When the alcohol vapor is used to strip or aid in stripping the ammonia from the reactor, additional or makeup alcohol can be added to the reactor at a rate to compensate for the vapor loss.

The reaction time is generally dependent on the aromatic polycarbamate being produced, the reaction temperature and pressure, the solvent and the catalyst optionally employed and will vary depending on whether the process is continuous or batch. It will normally not exceed 5 hours. Reaction times of less than 4 hours are common, and reaction times of 3 hours have been achieved without any problem.

If the alcohol and the organic solvent are present in such ratio that an azeotropic mixture is formed, the subsequent removal of any alcohol is greatly facilitated.

The process of the present invention may be conducted batchwise or as a semi-continuous or continuous process.

The polycarbamates of this invention may be employed in a number of commercial applications, for example as chemical intermediates. They may be converted to the corresponding aromatic polyisocyanates and alcohols by thermal decomposition or other methods described in the prior art.

EXAMPLES

Example 1

2 g 4,4'-diaminodiphenylmethane diamine (DADPM), 3.6 g urea and 25 ml 1-methoxy-2-propanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 3 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 1-methoxy-2-propanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 93-97% yield of the bis(1-methoxy-2-propyl carbamate).

Example 2

6 g 4,4'-DADPM, 10.8 g urea and 25 ml 1-methoxy-2-propanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 3 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 1-methoxy-2-propanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 98% yield of the bis(1-methoxy-2-propyl carbamate) and 2% of the monocarbamate.

Example 3

2 g 4,4'-DADPM, 3.6 g urea and 25 ml 2-ethoxyethanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 3 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 92-94% yield of the bis(2-ethoxyethyl carbamate).

Example 4

2 g 4,4'-DADPM, 2.43 g urea and 20 ml 2-methoxyethanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 2 hours. The alcohol was continuously added at a flow rate of 0.5

ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 90% yield of the bis(2-methoxyethyl carbamate).

Example 5

2 g polyaminopolyphenylmethane (pDADPM), 2.43 g urea and 24 ml 1-methoxy-2-propanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 2 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 1-methoxy-2-propanol was continuously vented off, in such a rate that the reaction volume was kept constant. FTIR analysis showed a 92% yield of the polyphenylmethane polycarbamate.

Example 6

2 g pDADPM, 2.43 g urea and 24 ml 2-ethoxyethanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 2 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. FTIR analysis showed a 90% yield of the bis(2-ethoxyethyl carbamate).

Example 7

2 g 4,4'-DADPM, 2.43 g urea and 20 ml 2-methoxyethanol were put together in a reaction vessel. The reaction mixture was heated at 190°C during 2 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 90% yield of the bis(2-ethoxyethyl carbamate).

Comparative example 1

2 g 4,4'-DADPM, 3.6 g urea and 23 ml butanol were put together in a

reaction vessel. The reaction mixture was heated at 190°C during 3 hours. Butanol was continuously added at a flow rate of 2.0 ml/min. and a mixture of ammonia and butanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 81-85% yield of the bisbutyl carbamate.

Comparative example 2

2 g 4,4'-DADPM, 2.4 g urea and 25 ml methanol were put together in a reaction vessel. The reaction mixture was heated at 200°C and under a pressure of 35bar during 3 hours. The alcohol was continuously added at a flow rate of 0.5 ml/min. and a mixture of ammonia and 2-ethoxyethanol was continuously vented off, in such a rate that the reaction volume was kept constant. HPLC analysis showed a 0.2 yield of the bis(2-methyl carbamate).

CLAIMS

1. A process for the preparation of an aromatic polycarbamate which comprises reacting an aromatic polyamine, urea and an alcohol, characterised in that the alcohol is an alkoxyated monoalcohol.
2. A process according to claim 1 wherein the alkoxyated monoalcohol has the formula $\text{CHR}^1\text{-(CR}^2\text{R}^3\text{-O)}_x\text{R}^4$ wherein x is an integer between 1 and 250 and $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ each are independently H or $\text{C}_1\text{-C}_{10}$ hydrocarbon radicals.
3. A process according to claim 1 or 2 wherein x is 1.
4. A process according to any of the preceding claims wherein the aromatic polyamine is selected from the group consisting of diaminodiphenylmethanes, toluenediamines, polyaminopolyphenylmethanes or mixtures thereof.
5. A process according to any of the preceding claims wherein the molar ratio of aromatic polyamine to urea is from about 1:1.2 to 1:10.
6. A process according to claim 5 wherein the molar ratio is from about 1:1.2 to 1:5.
7. A process according to any of the preceding claims wherein the alcohol is selected from the group consisting of 2-methoxy ethanol, 2-ethoxyethanol, 2-isopropoxyethanol, 1-methoxy-2-propanol, or mixtures thereof.
8. A process according to any of the preceding claims wherein the reaction temperature is in the range of from about 150 to 220 °C.
9. A process according to any of the preceding claims wherein the solvent is monochlorobenzene, ortho-dichlorobenzene, or mixtures thereof.
10. A process according to any of claims 1-9 wherein the reaction is carried out in the absence of an inert solvent.
11. A process according to any of the preceding claims which is carried out in the absence of a catalyst.

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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